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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : C09B 69/10, C02F 1/56	A1	(11) International Publication Number: WO 98/02492 (43) International Publication Date: 22 January 1998 (22.01.98)
(21) International Application Number: PCT/US97/12024 (22) International Filing Date: 11 July 1997 (11.07.97) (30) Priority Data: 682,497 17 July 1996 (17.07.96) US (71) Applicant: NALCO CHEMICAL COMPANY [US/US]; One Nalco Center, Naperville, IL 60563-1198 (US). (72) Inventors: WARD, William, J.; 23W305 Edgewood Court, Glen Ellyn, IL 60137 (US). CRAMM, Jeffrey, R.; 1017 Edwards Drive, Batavia, IL 60510 (US). REED, Peter, E.; 2280 North Weller Drive, Plainfield, IL 60544 (US). JOHNSON, Brian, S.; 1642C Country Lakes Drive, Naperville, IL 60563 (US). (74) Agent: KEEFER, Timothy, J.; Ladas & Parry, 224 South Michigan Avenue, Chicago, IL 60604 (US).		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZW, ARIPO patent (GH, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: DERIVATIZED RHODAMINE DYE AND ITS COPOLYMERS (57) Abstract Disclosed are the Rhodamine B esters of hydroxy C ₂ -C ₆ lower alkyl acrylates. Specifically, the hydroxy lower alkyl radical is a linear hydroxy lower alkyl radical having the hydroxy group attached to the terminal carbon atom. Also shown are copolymers of diallyldimethyl ammonium chloride which contains from 0.01-2 mole percent of these Rhodamine B esters and their use in treating industrial waters.		

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DERIVATIZED RHODAMINE DYE AND ITS COPOLYMERSBACKGROUND OF THE INVENTIONField of the Invention

This invention relates to Rhodamine B which is modified to contain a vinyl group and its incorporation into radically polymerized compounds such as diallyldimethylammonium chloride (DADMAC) polymers.

Description of the Prior Art

Technological advances have made it economically practical to monitor the residual level of polymeric coagulants in wastewater effluents. Knowledge of the fate of coagulants has several advantages:

- 1) monitor treated water residuals,
- 2) control coagulant addition, and
- 3) elucidate coagulation mechanisms.

This allows better control of dosage levels of these coagulants and to minimize these polymers contributing to pollution. A common approach to monitoring the level of water soluble polymer coagulants has been, to blend fluorescent dyes in small amounts and to use fluorescence of the mixture to determine the concentration of the polymer in aqueous systems.

This approach has met with some success but it has limitations. In using simple blends of fluorescent dyes with polymeric coagulants there is the problem that the dye associates itself with other components, such as particulates. Subsequent fluorescent detection of the dye does not provide the location of the polymeric coagulant. A more recent approach has been to covalently modify the dye

so that it might be incorporated by means of chemical reaction into the polymer. Since the dye and the coagulant are physically attached, detection of the dye also detects the coagulant polymer. While this approach has met with some success, it is economically important that the dye be readily detected at low concentrations. Particularly there is not presently available a DADMAC polymer which contains chemically combined therewith a fluorescent dye suitable for monitoring these polymers when they are used in aqueous systems.

If it were possible to modify polymers with a highly fluorescent dye, so that the dye became a part of the molecule and that the so modified polymer could be readily detected in the part per billion (ppb) range using existing fluorescent detection techniques, an advance in the art would be afforded. Also of importance would be, to use in the modification of the polymers, a dye which was easily synthesized from available chemicals, was stable and retained a high degree of fluorescence. Finally, the modified polymer should have activity as a water treating chemical corresponding to the activity of a similar unmodified polymer.

SUMMARY OF THE INVENTION

The invention comprises the Rhodamine B ester of a hydroxy C_2-C_6 lower alkyl acrylate. The hydroxy lower alkyl radical preferably, is a linear hydroxy lower alkyl radical having the hydroxy group attached to the terminal carbon atom. In another preferred embodiment, the Rhodamine B ester is a hydroxy lower alkyl radical is a C_2-C_4 radical, an example of which is the Rhodamine B ester of 4-hydroxybutyl

acrylate. The important point is that the hydrocarbon linkage contain a hydroxy group and an acrylate group. The hydroxy group for modification of Rhodamine B, and the acrylate group for free radical polymeric incorporation.

The invention also comprises copolymers of diallyldimethyl ammonium chloride which contains from 0.01 - 2 mole percent of the Rhodamine B esters of the types described above. It is noted that any free radical polymerization process could incorporate the invention as long as the dye's fluorescent properties were retained. The invention further contemplates using these polymers in water treating applications such as, but not limited to, coagulation. This allows the dosage and residual quantities of the polymers to be controlled and monitored using conventional fluorescence detecting equipment even though the polymers are present in the ppb range.

THE DRAWINGS

Figure 1 shows a scheme for reacting Rhodamine B with 4-hydroxy butyl acrylate.

Figure 2 illustrates the polymerization of DADMAC with the modified Rhodamine B of Figure 1.

Figure 3 demonstrates the ability of a DADMAC-Rhodamine B copolymer to act as a coagulant and be easily detectable at low dosages.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Modified Rhodamine B and its DADMAC Copolymers

Rhodamine B is a well known fluorescent dye with its structure being shown in Figure 1. 4-hydroxy butyl acrylate is a well known acrylate ester and is commercially

available. While this ester is preferred other acrylate esters that may be used in the practice of the invention are 2-hydroxy ethyl acrylate and 6-hydroxy hexyl acrylate and the like. The hydroxy acrylate esters are desirably reacted with the carboxylic acid group of the Rhodamine B at low temperatures such as at about room temperature ± 24 degrees C using the synthetic methods generally described in the publications: Tetrahedron Letters No. 46 pp 4775-8, Pergamon Press, 1978 and Euro Polymer J. Vol. 27 No. 10 pp 1045 and 1048. The disclosures of these references are incorporated herein by reference.

The DADMAC polymers modified by the acrylate ester modified Rhodamine B may be synthesized using known free radical polymerization techniques. These copolymers may contain between 0.01 to 2 mole percent of the modified Rhodamine B monomer based on DADMAC. Of course, the invention is in and of itself, a monomer and potentially could be incorporated at higher levels. Preferably the amount of the fluorescent monomer is within the range of 0.1 to 1 mole percent. The modified or tagged DADMAC polymers have an intrinsic viscosity, as measured in 1M NaNO₃ at 30 degrees C., of at least 0.3. For most water treating applications such as coagulation the intrinsic viscosity should be within the range of 0.3 to 0.9. For some applications the intrinsic viscosity may be 1.6 or greater. When used to treat industrial waters the dosage of the modified polymers would usually vary from a few parts per million up to several hundred depending on the system treated and the intrinsic viscosity of the polymer used. When used as a coagulant the dosage would typically be between a few ppm up to ca. 100 ppm.

EVALUATION OF THE INVENTION

Synthetic Procedure: 4-Hydroxybutylacrylate/Rhodamine B Ester

The following procedure was used to prepare this material in the laboratory and is shown in Figure 1. To a 100 mL round bottom flask, equipped with a magnetic stirring bar, was added 3.00g (6.26 mole) of Rhodamine B (97%) and 40 mL of anhydrous methylene chloride solvent. The mixture was stirred, under nitrogen, until the Rhodamine reagent was dissolved. An amount (0.08g, 0.65 mole) of 4-dimethylaminopyridine (DMAP) was then added to the flask, along with 1.5 mL (1.6 equivalents) of 4-hydroxybutylacrylate (HBA, 96%). The mixture was then cooled to 0 degrees C, and 6.26 mL of 1,3-dicyclohexylcarbodiimide (DCC, 1.0 M solution in methylene chloride, 1 equivalent) was injected into the reaction flask with stirring. The reaction was held at 0 degrees C for 1/2 hour, then the reaction was allowed to slowly warm to room temperature, and then stirred under nitrogen overnight. It was noted that the reaction by-product dicyclohexylurea (DCU) began to precipitate from solution shortly (approximately 3 minutes) after the addition of the DCC.

At the end of the reaction period the methylene chloride solvent was removed via rotary evaporation, and the reaction mixture re-dissolved in 50 mL of acetonitrile. The insoluble DCU was filtered off and the solvent removed and the product dried under a vacuum, leaving an amorphous solid, that is soluble in water and most polar organic solvents. The product also has the characteristic of an extremely powerful dye. Some impurities were removed by passing the material through a silica gel plug (70-270 mesh)

using an acetonitrile mobile phase. In this way 1.6g of the dye was isolated (molecular wt. = 605.19 amu). Thin layer chromatography (TLC) showed the presence of three spots, two are weak and one is strong. The strong spot corresponds to the product. A weak spot below the product spot corresponds to unreacted Rhodamine B. A weak spot above the product spot is unknown, it may be due to dimerized product. All the spots seemed to be fluorescent. The TLC solvent that gave the best separation was isopropyl alcohol. NMR analysis gave rise to complex spectra that indicated that the ester product was formed. The purity was approximately 90%. The major impurities were approximately 5% unreacted Rhodamine B reagent and 5% of an unknown compound.

Synthetic Procedure: Tagged DADMAC Polymer

The following laboratory method was used to prepare a DADMAC polymer containing the above Rhodamine acrylate dye monomer and is shown in Figure 2. Into a 250 mL reaction kettle equipped with a stirring shaft, thermocouple, condenser, nitrogen inlet, and an addition port, was added 0.28g (0.13 mole percent based on monomer) of the dye monomer (approximately 90% pure) and 5.16g D.I. water. To this was added 80.64g of a 62.0% DADMAC monomer solution. The mixture was stirred and purged with nitrogen. A quantity of 18.0g of NaCl was added to the mixture and the reaction mixture heated to 58 degrees C in a water bath. An initiator solution was prepared by dissolving 0.50g of V-50 initiator into 5.00g of D.I. water. One mL of this initiator solution was then injected into the reactor, and a timer was started. After one hour another 1 mL portion of the initiator solution was added to the reactor, and again at the two hour and three hour mark. At this point the

mixture was a very thick paste. After 4.5 hours the polymer began to climb up the stirring shaft. When the timer reached 5 hours, 40 mL of D.I. water was added to the mixture, then an additional 17 mL of water was added at 5.25 hours. The reaction temperature was then raised to 80 degrees C, and the remaining 1 mL of the initiator solution was injected into the reactor. The mixture was then held at 80 degrees C with stirring for one hour. The reactor was removed from the water bath and 83g of D.I. water was added with stirring. The mixture was allowed to cool and another 83g of water was added to the reactor to give a 15% polymer solution. The product produced was a viscous dark pink material.

The following procedures were used to characterize the polymer. The Brookfield viscosity was obtained using a #2 spindle at a speed of 12. The intrinsic viscosity (I.V.) was taken on a 1% polymer solution prepared from 6.67g of polymer product, 50 mL of 2M NaNO_3 , 1 mL of 1M sodium acetate solution, and diluted to 100 mL with D.I. water. Dialysis experiments were performed using a 12,000 - 14,000 MW cut-off membrane. Standard techniques were employed. The polymer product was precipitated and isolated by adding a small amount of the product to a large volume of acetone. The resulting gel was isolated and dissolved in a small amount of methanol. Any insoluble solids were filtered off, and the methanol polymer solution added to a large volume of acetone. The precipitated polymer was collected, washed, and dried under a vacuum. The dye monomer was incorporated into the dye at 0.13 mole percent (based on DADMAC monomer, assuming a dye monomer purity of 90%), or 0.08% by weight of product. About 99% incorporation of the dye into the

polymer was achieved. Total polymer solids of the tagged polyDADMAC was measured at 15%. The synthesized tagged polymer had the following characteristics set forth in Table I.

TABLE I

	Tagged pDADMAC	pDADMAC
Appearance:	Deep Red/Pink Color	Clear White
Brookfield Viscosity:	1363 cps	990 cps
I.V.:	1.0 dL/g	1.03 dL/g
pH:	4.85	4.68
Wt. Average MW:	890,000	475,000
Number Average MW:	70,000	32,000
Polydispersity:	12.7	14.8
Polymer Solids:	15% (theo.)	14.97

Except for the color, tagged pDADMAC has similar characteristics to un-tagged pDADMAC. PolyDADMAC dye incorporation was determined analytically. The polymer remained colored after precipitation and washing. The polymer was also placed in a 12,000 - 14,000 dialysis membrane and dialyzed with D.I. water for 48 hours. Only a small amount of color was observed to pass out of the membrane. The material in the membrane was bright pink. A control experiment was done, in which, the dye monomer was blended with a sample of un-tagged pDADMAC. In this case practically all of the dye seemed to pass through the membrane leaving the un-tagged polymer behind. Analysis

indicated that there were about 9 ppm of residual tagged monomer in the tagged polymer.

Detection Limits

Lower detection limits are desirable for several reasons. Lower detection limits allows formulators to use lower dye levels in new products. For control purposes, a dye-tagged molecule requires detection without changing product properties. Finally, for tagged polymer detection, the higher the dye molecule fluorescence sensitivity, the lower the detection limit. This last point is important for answering the question of polymer residuals in treated waters. Fluorescence sensitivity is defined as:
Fluorescence Sensitivity = extinction coefficient x Quantum Yield

From Table II it is shown the modified Rhodamine has a higher Fluorescence Sensitivity than Rhodamine B. By modifying Rhodamine B we get two distinct advantages over Rhodamine B: high fluorescence sensitivity and the ability to incorporate the dye into free-radical polymerization reactions. For tagged pDADMAC, the detection limit was determined to be 50 ppb using standard fluorometry techniques. It could be as low as 10 ppb.

TABLE II

	Absorption Peak	Extinction Coefficient (1-mol/cm)	Relative Quantum Yield*
Rhodamine B	555	110,000	0.62 (absolute)
Modified Rhodamine B	560	88,500	0.96

Tagged polyDADMAC	585	181	0.425
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*Rhodamine B has an absolute Quantum yield of 0.62.

Stability

Since the Rhodamine B modified polymers is formed by free radical polymerization via chemical reaction of an acrylate onto the carboxphenyl moiety, the reverse hydrolysis reaction would remove the dye moiety. Consequently, the acrylate group's stability to hydrolysis is important. The modified Rhodamine B-acrylate monomer was subjected to potential hydrolysis conditions and using chromatography to determine the free Rhodamine B (residual and from hydrolysis), the monomer, and any other hydrolysis products. Results showed that at pH 7 and low monomer concentration (1-20 ppm), about 15 - 20% of the tagged monomer were hydrolyzed after 28 days at room temperature without exposure to light. However, high monomer concentration (800 ppm) solution appeared to be stable up to 4 weeks at room temperature without exposure to light. It is predicted that the dye monomer's hydrolysis rate will be slower when it is attached to a polymer, due to possible steric constraints.

Tagged Polymer Activity

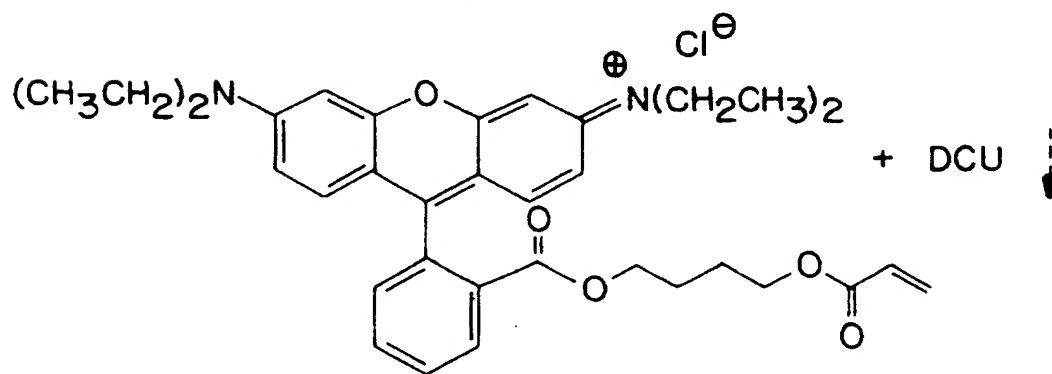
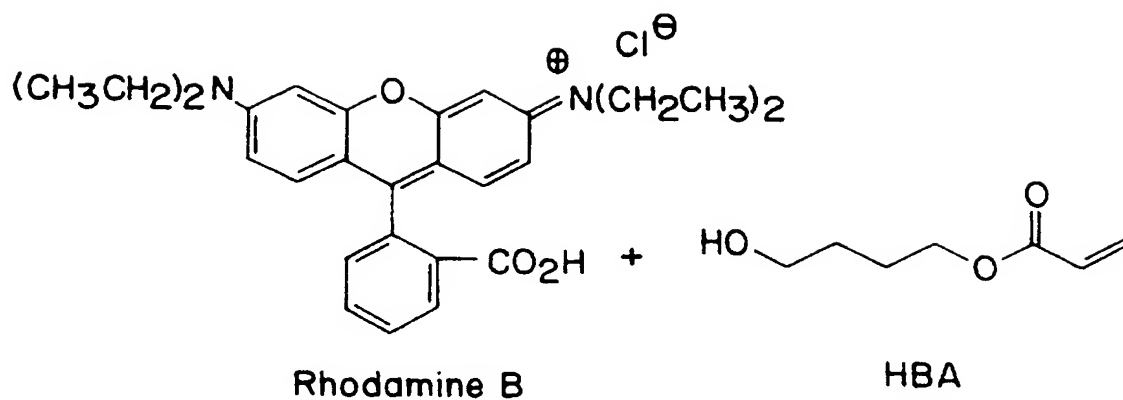
Aeration Basin effluent wastewater from a refinery was used for activity testing. Figure 3 shows that tagged polyDADMAC has activity. This result proves that chemically tagging pDADMAC does not inhibit coagulation power. Activity was measured in NTUs (Nephrolytic Turbidity Units).

CLAIMS

1. The Rhodamine B ester of a hydroxy C_2-C_6 lower alkyl acrylate.
2. The Rhodamine B ester of claim 1 where the hydroxy lower alkyl radical is a linear hydroxy lower alkyl radical having the hydroxy group attached to the terminal carbon atom.
3. The Rhodamine B ester of claim 1 where the hydroxy lower alkyl radical is a C_2-C_4 radical.
4. The Rhodamine B ester of 4-hydroxy butyl acrylate.
5. A copolymer of diallyldimethyl ammonium chloride which contains from 0.01 - 2 mole percent of the Rhodamine B ester of claim 1.
6. The copolymer of claim 5 where the Rhodamine B ester is the ester of claim 2.
7. The copolymer of claim 5 where the Rhodamine B ester is the ester of claim 3.
8. The copolymer of claim 5 where the Rhodamine B ester is the ester of claim 4.
9. A method of treating industrial waters with diallyldimethylammonium chloride polymers to control and monitor the dosage and presence of these polymers by means of fluorescence detection which comprises using the diallyldimethylammoniumchloride fluorescent copolymer of claim 5.
10. The method of claim 9 where the diallyldimethylammoniumchloride copolymer is the copolymer of claim 6.

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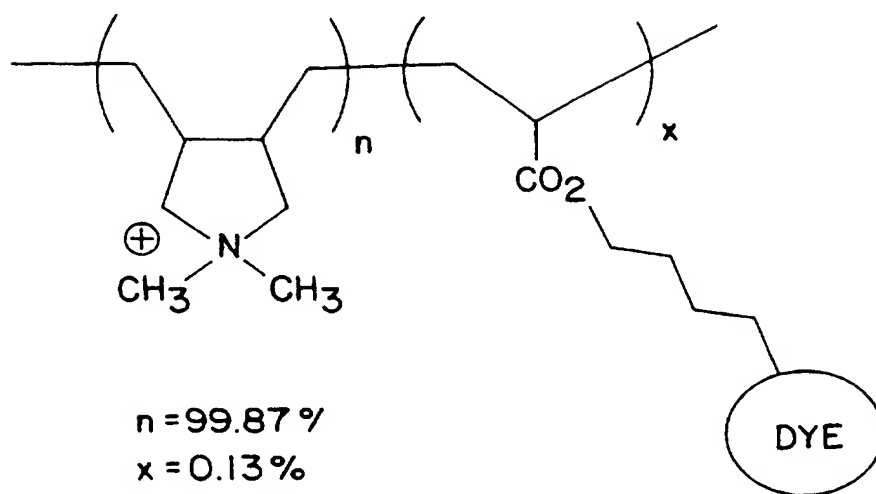
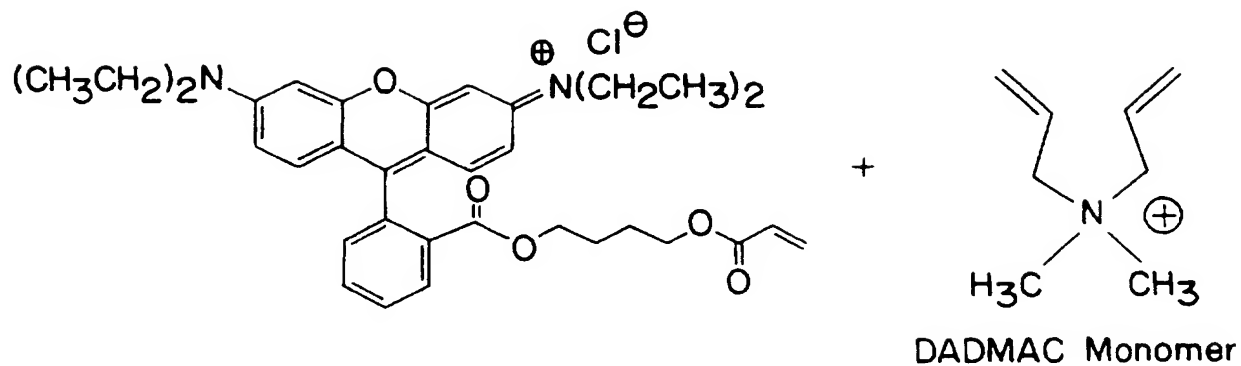
FIG. 1



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FIG. 2

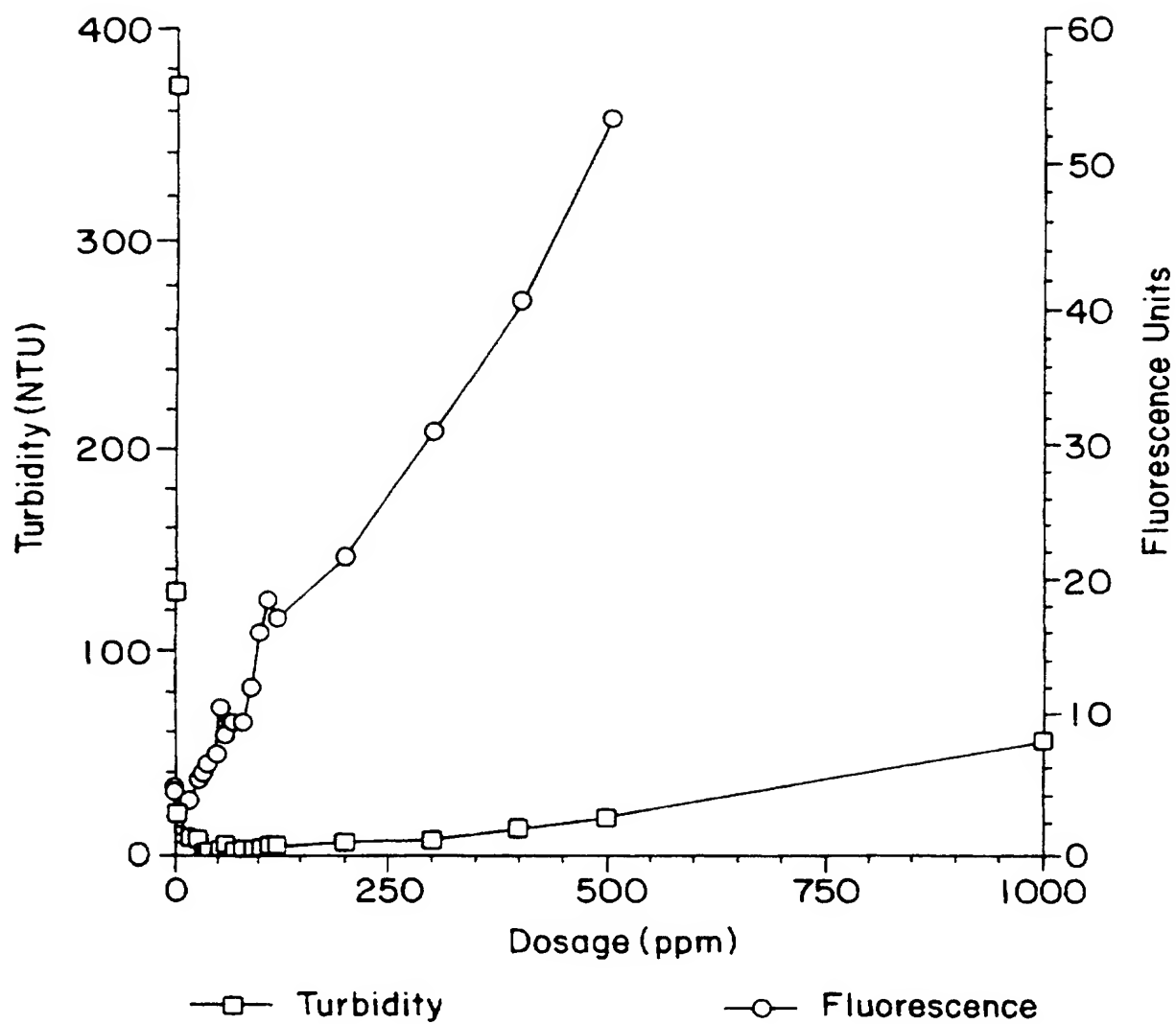


TAGGED DADMAC POLYMER

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FIG. 3



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INTERNATIONAL SEARCH REPORT

National Application No
/US 97/12024

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C09B69/10 C02F1/56

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C09B C02F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 228 868 A (ALLIED COLLOIDS LTD) 15 July 1987 see claims ---	1-10
A	EP 0 203 761 A (ALLIED COLLOIDS LTD) 3 December 1986 see claims; example ---	1-10
P, A	WO 97 04510 A (CONSEJO SUPERIOR INVESTIGACION ; COSTELA GONZALEZ ANGEL (ES); GARCI) 6 February 1997 see page 4, line 13 - page 10, line 15; claim 1 -----	1-3

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

5 December 1997

Date of mailing of the international search report

17/12/1997

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Information on patent family members

International Application No

PCT/US 97/12024

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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WO 9704510 A	06-02-97	NONE	

Form PCT/ISA/210 (patent family annex) (July 1992)



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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification⁶ :

C09B 69/10, C02F 1/56

A1

(11) International Publication Number:

WO 98/02492

(43) International Publication Date:

22 January 1998 (22.01.98)

(21) International Application Number: PCT/US97/12024

(22) International Filing Date: 11 July 1997 (11.07.97)

(30) Priority Data:

08/682,497

17 July 1996 (17.07.96)

US

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Michigan Avenue, Chicago, IL 60604 (US).(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR,
BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE,
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*(Referred to in PCT Gazette No. 14/1998, Section II)

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